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# Photoluminescence in Tagging: A Glowing Review

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## **Abstract**

This literature review explores the options of using photoluminescence for tagging uranium fuel and zirconium cladding in order to easily and quickly associate interdicted material to its facility of origin or pathway after loss of institutional control. Photoluminescence is the spontaneous emission of radiation by a substance when excited by interaction with light. The source of photoluminescence can be from organic, inorganic, and organometallic compounds. Each luminophore, or compound responsible for luminescent properties, has individual strengths and weaknesses, depending on the intended use. Many factors can affect the brightness, lifetime, color, and detectability of luminophores, such as humidity, temperature, oxygen availability, noise from radiation-induced luminescence, and the presence of quenching substances like iron. Application of luminescent compound to the surface of an item can be done using paint, dye, thin film, thick film, or electrochemical coating. Several of the application techniques may have secondary functions such as corrosion resistance and detection, heat resistance, protective properties, and more. When considering cladding, there are various successful studies on the application of luminescent coatings on zirconium. However, significant research will be necessary to explore which luminophore and which application technique would best fit the intended use. In order to proceed with this research, a baseline of the natural luminescence of the intended base material (nuclear fuel or cladding) is necessary. While there may be issues with background noise, quenching from the environment, quenching from the substrate, signal to noise weakness, etc. the multitude of options may make photoluminescent tagging an option. In summary, this review has demonstrated that photoluminescence is a potential option to tag nuclear fuel and cladding, but additional paper-studies, testing, and research is required to understand the compatibility of luminescent tags in nuclear reactor environments, manufacturability, and detectability.

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## 1. Introduction

When considering uses for luminescence, the first things that could come to mind are fingerprint dusting on crime shows or the cashier shining a light on your hundred dollar bill at the grocery store. This literature review applies these same concepts to explore the use of luminescent tagging on uranium fuel and cladding at its manufacturing source. Tagging nuclear fuel allows for the ability to trace fuel provenance in the event the material is lost and then interdicted. There are many possible tagging methods, including mechanical, material property changes, chemical, etc. Luminescent tags, either in a standalone capacity or in concert with other tags, can provide a unique (and therefore less able to be spoofed) method to improve traceability of high-value items.

The purpose of this review is to investigate the possibilities of tagging metallic and ceramic surfaces with photoluminescent materials. First, the phenomenon of luminescence will be described, along with where photoluminescence comes from. The tagging techniques and examples of those techniques are then explored. Pertinent attributes of each technique are summarized in a stoplight chart and then discussed regarding nuclear fuel and cladding applications.

A survey of specific end-use scenarios is beyond the scope of this document; additional evaluation of specific material and detection choices as well as research and development is needed.

## 2. What is luminescence?

Luminescence is the spontaneous emission of radiation by a substance that is not caused by heat [2012val]. There are many forms of luminescence that relate to the timing or cause of excitation, and Table 1 illustrates those interactions.

Table 1. Types of Luminescence.

<b>Mechanism of Luminescence</b>	<b>Type of Luminescence</b>
Chemical Reaction	Chemiluminescence <ul style="list-style-type: none"><li>• Bioluminescence</li><li>• Electrochemiluminescence</li></ul>
Crystallization	Crystalloluminescence
Electricity	Electroluminescence <ul style="list-style-type: none"><li>• Cathodoluminescence</li></ul>
Mechanical Action	Mechanoluminescence <ul style="list-style-type: none"><li>• Triboluminescence</li><li>• Fractoluminescence</li><li>• Piezoluminescence</li></ul>
Sound	Sonoluminescence
Absorption of light	Photoluminescence <ul style="list-style-type: none"><li>• Fluorescence</li><li>• Phosphorescence</li></ul>
Ionizing Radiation Interaction	Radioluminescence

Photoluminescence is a type of light-matter interaction as shown in Figure 1. When certain substances are hit with radiation like X-rays or ultraviolet (UV) light, electrons in that substance are temporarily excited into a higher energy state. The electron may then relax via non-radiative transitions into a lower excited state before returning to the ground state by emitting a photon. Because the electron relaxed into a lower energy excited state, the photon emitted is at a lower energy and a longer wavelength than the exciting photon (Figure 2).

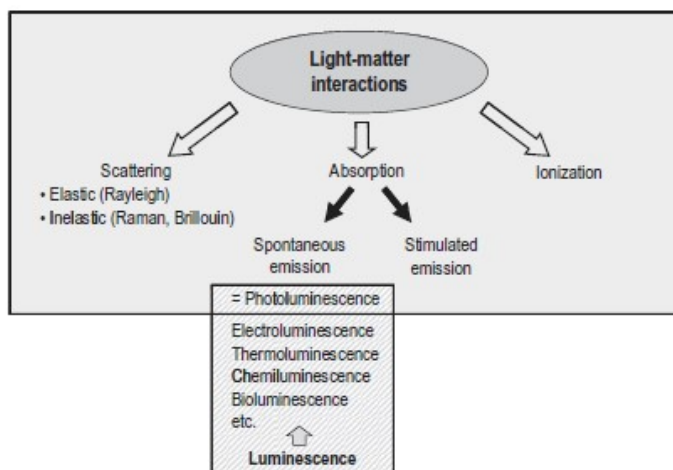


Figure 1. Illustration of photoluminescence in the frame of light and matter interaction [2012bre].

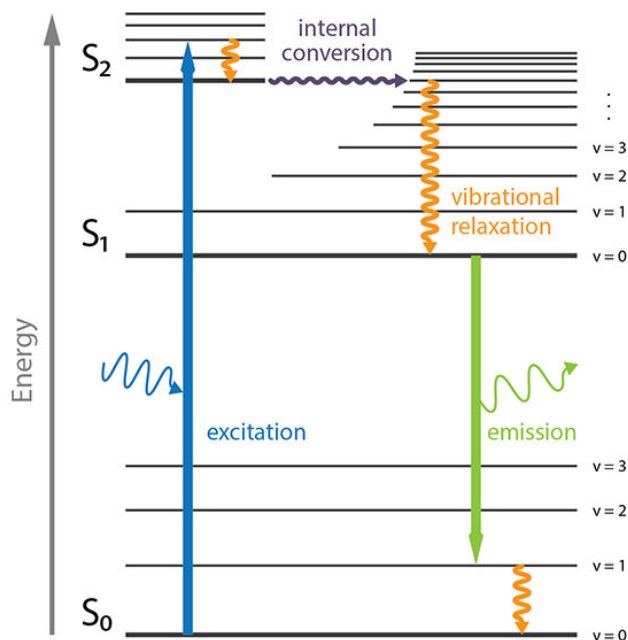


Figure 2. Simplified Jablonski Diagram showing fluorescence. Here an electron absorbs a photon, jumping to  $S_2$ , an excited state. It relaxes into the  $S_1$  lowest excited state before emitting fluorescence by releasing a photon of a lower energy than the exciting photon, and then returning to ground state  $S_0$  [2019poh].

This review focuses on two types of photoluminescence, fluorescence and phosphorescence, which can be activated quickly and easily using a UV lamp at atmospheric pressure and temperature. The difference between fluorescence and phosphorescence is often connected to time. Fluorescence is considered light emission from a substance *while* exposed to exciting radiation, such as in black light reactive paint, whereas phosphorescence continues glowing *after* the excitation has ceased, such as in glow in the dark paint. However, the actual difference between the two types of luminescence lies in the electron spin. In a relaxed state, two electrons in a single orbital have opposite spins. When an electron moves to an excited state due to absorption of a photon, the electron maintains the spin orientation, forming a singlet excited state. In fluorescence the relaxation events from  $S_1$  to  $S_0$  are spin neutral, where the orientation of the electron remains the same at all times. In phosphorescence, electron spins invert in a process called “intersystem crossing” where electrons move from a singlet excited state ( $S_1$ ) to an energetically favorable triplet excited state ( $T_1$ ) (Figure 3). This move causes an inversion of the electron spin. In the triplet excited state, both electrons can be moving parallel to one another, rather than opposite. The triplet excited state is metastable, which means that there can be a delay in relaxation, emission of a photon, and thus phosphorescence.

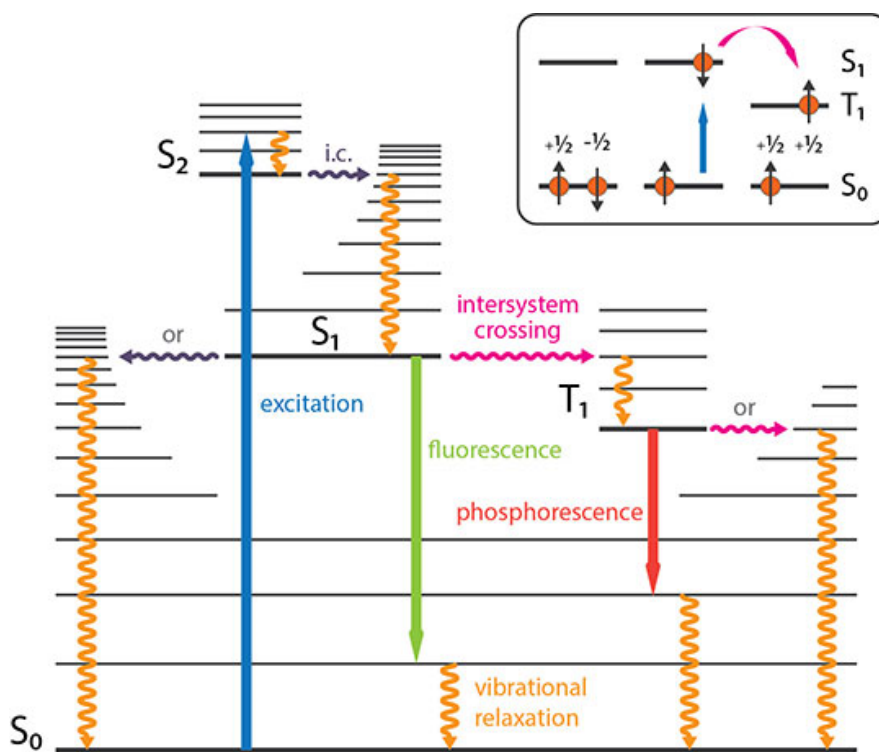


Figure 3. Simplified Jablonski Diagram showing the difference between fluorescence and phosphorescence. In phosphorescence, there is intersystem crossing into excited triplet state ( $T_1$ ), and the spin of the involved electron is flipped. The resulting triplet state is metastable and relaxation may be delayed [2019poh].

An easily observable example of luminescence is fluorescent minerals like fluorite, calcite, aragonite, zircon, etc. When hit with a UV light, the impurities or “activators” in these minerals cause the mineral to fluoresce. The amount or type of activators within the mineral controls the color of the luminescence. Technically, nearly any mineral can become luminescent if it contains the activators in its crystal structure. Conversely, while there are luminescent activators, there are also quenchers, which diminish or change luminosity.

### 3. Sources of photoluminescence

According to [2012val], there are three basic types of compounds which produce photoluminescence. These are as follows:

1. *Organic compounds*-aromatic hydrocarbons like naphthalene, dyes like fluorescein and rhodamine, polyenes, diphenylpolyenes, some amino acids like tryptophan and tyrosine, etc.
2. *Inorganic compounds*-, lanthanide ions like  $\text{Eu}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Ho}^{3+}$  and  $\text{Pr}^{3+}$ , glasses doped with Nd, Mn, Ce, Sn, Cu, Ag,  $\text{Al}_2\text{O}_3/\text{Cr}^{3+}$ , crystals like ZnS, CdS, ZnSe, CdSe, GaS, GaP, semiconductor nanocrystals (CdSe), Ce doped yttrium aluminum garnet (YAG), metal clusters, carbon nanotubes, some fullerenes, uranyl ions ( $\text{UO}_2^{2+}$ ) as incorporated impurities, rare earth elements Pr, Nd, Ho, Er, and Yb are all fluorescent, while Sm, Eu, Gd, Tb, Dy, and Tm are phosphorescent.
3. *Organometallic compounds*-porphyrin metal complexes, Ru complexes, Cu complexes, lanthanide ion complexes, etc.

As this report is discussing the application of photoluminescence to tagging of metallic fuel and cladding, it is worth mentioning that the taggant must occur in a ceramic or ionic state, not in the metallic state. The metallic state as it may be present in some of the above materials is not photoluminescent. However, metals may be coated with photoluminescent oxides and other ceramics, , etc.

Important to note for nuclear fuel applications is that uranyl ions are luminescent, and the transitions occur at about 420 nm under a UV light. This falls within the range of visible light on the electromagnetic spectrum (Figure 4). Compounds containing the uranyl ion can be orange, as in fiestaware, but can also be red, yellow, or green. “Vaseline glass” and other 1930s Depression-era and earlier glassware were colored with uranyl ions and can easily be identified by their fluorescence under black light.



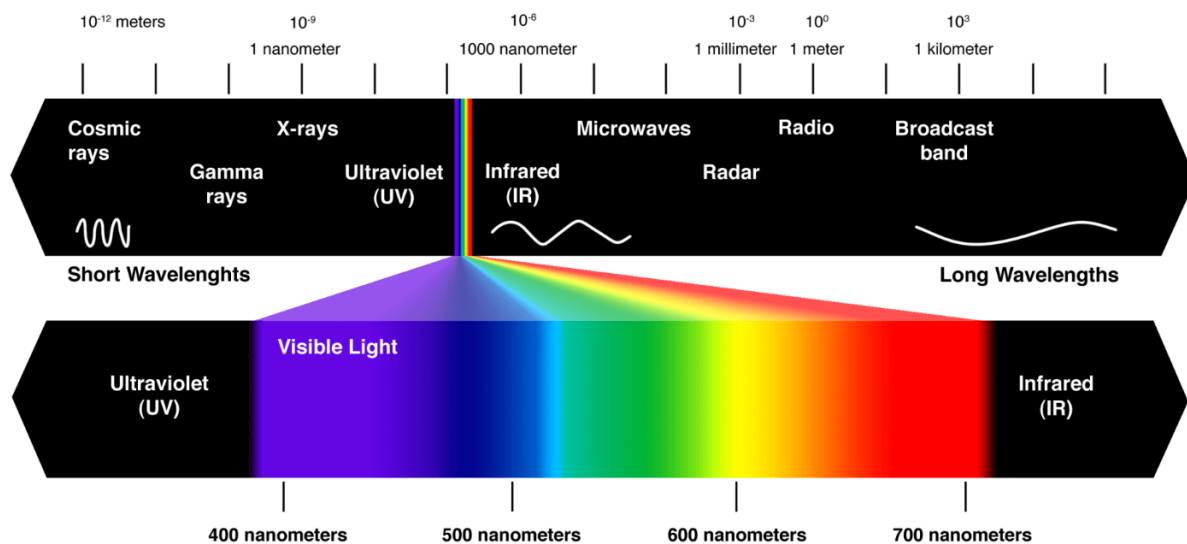


Figure 4. Electromagnetic spectrum with the visible light spectrum in color [2020onc]. For reference, UV light is from 10-400 nm, but the typical UV “black” light is 365 nm.

As mentioned in point two, the lanthanides can increase likelihood of luminescence, such as Sm being a good phosphorescent activator. However, some metals can also quench luminescence. Quenching decreases luminescence or can stop luminescence altogether. Metals like Fe, Pt, Pd, Co, Ni, Cu, Hg, Cr, and other factors like temperature, presence of water, Cl, lack of O, or iodide can quench luminescence in a material [2012val]. The quenching effect can influence which compounds are best for tagging which substrate.

#### 4. Tagging Techniques

Due to the variety of compounds, ions, and materials that can be luminescent, there are several ways to incorporate luminescence into the manufacturing process. In the following subsections, five surface application method to impart luminescent tags are considered; 1) coatings using fluorescent dyes, 2) paints and pigments, 3) thin films, 4) thick films and coatings, 5) plasma electrolytic coatings. Additional processes may be available, but the presented selections are considered to be relevant specifically to the topic of nuclear fuel tagging.

##### 4.1. Coatings using fluorescent dyes

Organic fluorescent dyes are commonly used for biologic tracing purposes, but have also been used to detect corrosion. Zhang [1999zha] used a clear acrylic paint mixed with fluorescing 7-hydroxycoumarin or coumarin pH indicators on 5454 Al. The project focused on sensing cathodic reactions under coatings in localized corrosion such as pitting, crevice, and exfoliation corrosion using a

modified paint for aircrafts. The indicators were added in concentrations from 0.1-2.4 wt%. Color changes and fluorescing were detected by the naked eye.

Liu [2010liu] used an epoxy-polyamide coating on 2024-T4 Al and 1018 steel with 7-AMC and 7-DMC indicators/phosphors respectively to indicate symptoms of corrosion. The concentrations of the fluorescent indicators in the coating ranged from 0.05-1.5 wt%. The indicators changed from fluorescent or to fluorescent depending on the oxidation state/change in pH/interactions with metal ions like  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ . Liu further tested the long-term stability of the indicators through exposure to air and under UV exposure. After three years of exposure to air, there were no changes in the fluorescence, and after 15 hours straight of UV exposure, there was no visible fluorescent quenching. These results indicate that a tag of this type would be shelf stable, and likely to persist, at the original strength, over a period of storage. Experimentation during this project also showed that 80 microns was the optimal thickness of coating that kept the necessary fluorescent intensity while still adhering to the metal substrate.

Fluorescent dyes may not be the best choice for nuclear fuel and cladding because organic compounds are sensitive to the high temperatures (300°C) and ionizing radiation. More inorganic options will be considered next.

#### 4.2. Paints and Pigments

The luminescent compounds in pigments are generally inorganic. These compounds can be used like ink or paint when mixed with epoxy or acrylic paint. The phosphor particles are dispersed as microscopic particulates in the medium, rather than dissolved. Jaiswal and Haranath [2021jai] used  $\text{CaAl}_2\text{O}_4\text{:Eu}^{2+}\text{Nd}^{3+}\text{Si}^{4+}$  phosphor powder to create an ink using epoxy-based colloidal suspension. This ink was created to produce concealed patterns on goods and certificates using QR code patterns. Under a standard 365 nm UV light, the ink emits in the visible part of the light spectrum, but was invisible to the unaided eye. The production of this powder suspension is rather complicated where the stability of the powder was dependent on the process of mixing, temperature, relative humidity, pH, and concentration of powder and epoxy. The mixing had to be carried out at room temperature for 3 or more hours in a dust-free and dry environment.

Another security-focused project created inks out of  $\text{Yb}^{3+}/\text{Er}^{3+}/\text{Tm}^{3+}$  doped  $\beta\text{-NaYF}_4$  nanoparticles with oleic acid as the capping agent in toluene to create QR codes [2012mer]. QR codes were printed using Optomec direct-write aerosol jetting onto glass, paper, and Kapton (Figure 5). This project used a mix of phosphors which did not have overlapping luminescent wavelengths, thus creating a two-part luminescent QR code. The main QR code was one color, but another covert code was printed within the QR code in a different distinguishable color. Under normal light, the ink was invisible, but is detectable by the unaided eye after using near-IR laser excitation. The QR code could be scanned by a smart phone. On a glass slide the thickness of the ink layer was 1.5  $\mu\text{m}$ .

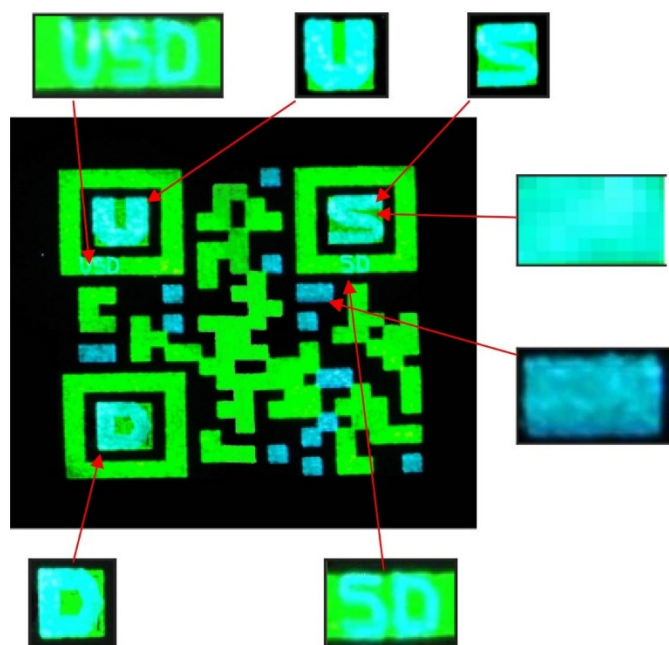


Figure 5. Image of the two color luminescent ink printed as a QR code with “USD,” “U,” “S,” “D,” and “SD” printed in ink that luminesces blue over the ink that luminesces green [2012mer].

Though the previous studies show much promise in the simplicity of use and the invisibility to the naked eye, production of nanoparticle-based inks and paints may not be the simplest or cheapest methodology. Also, Bite and others mentioned that this technique has low efficiency and weak adhesion when applied to metals [2018bit].

#### 4.3. Thin films

A thin film is a layer of materials ranging from fractions of a nanometer to several micrometers thick. Commonly, luminescent thin films are used for flat-panel displays, solar cells, optics systems, etc. Luminescent thin films, as opposed to powder coatings, have relatively good thermal stability, reduced outgassing, and better adhesion to the solid surface [2013zha]. The luminescent thin films can be deposited using pulsed laser deposition (PLD), sputtering, molecular beam epitaxy (MBE), spray pyrolysis, sol-gel, among others. A thin film can be made luminescent by doping with two types of metal ions as impurities: transition metal ions and lanthanide ions. In most applications, a thin-film luminophore is made up of a crystalline host and intentionally incorporated chemical impurities in low concentrations. Spray pyrolysis is probably the cheapest, easiest, and fastest way to deposit a thin film on a large area as it does not require vacuum.

Through a project focused on using ZnO in piezoelectric applications [2015lin], Lin et al. offer some insight on depositing ZnO thin films onto various metal substrates. The project focused on using radio frequency magnetron sputtering to deposit ZnO thin films onto Au, Pt, and Al substrates. The project found that the ZnO deposited onto Al was the best crystalline structure but had the highest

surface roughness. The grain size of the deposited ZnO ranges from 10 to 20 nm. The sputtering pressure influences the grain size and roughness of the depositional layer, and 1.0 Pa was found to be the best pressure for this system.

Wang et al. [2007wan] used simple wet chemistry to grow ZnO nanosheet film on an aluminum substrate. The work suspended the aluminum substrate in a Teflon-lined autoclave filled with an equimolar aqueous solution of zinc nitrate hydrate and methanamine at constant temperature of 90°C for 3 hours, then dried in air at 60°C. The thin film exhibited a strong orange photoluminescence, stronger emission than a ZnO film formed by DC reactive magnetron sputtering.

Winer and others [1986win] created thin uranium oxide films by exposing high-purity polycrystalline uranium surfaces to small amounts of pure H<sub>2</sub>O, dry O<sub>2</sub>, or CO between 85 and 300 K. The study found that the oxidized surfaces exhibited uniform faint blue luminescence at 400nm. There were a few samples in the study emitted a secondary red luminescence at about 800 nm. This secondary luminescence was believed to be formed due to localized concentrations of oxide or specific oxygen species on the surface. The use of thin uranium oxide films is anticipated to be one area of significant promise for use in nuclear fuel applications, and it is possible that both uranium-based ceramic and metallic fuel forms already have an intrinsic luminescence. Prior to undertaking studies aimed at tuning or adjusting luminescence in nuclear fuels, a baseline study is recommended to assess the intrinsic luminescence.

#### **4.4. Thick films and coatings**

In this review, thick films and coatings are considered the same or similar. A thick film is approximately 100+  $\mu\text{m}$ . Thick films can be deposited in some similar ways as thin films including sol-gel and spray pyrolysis. Thick films can also be applied using thermal spraying and plasma spraying. Thermal barrier coatings (TBC) are one version of thick films. TBCs are usually applied to metallic surfaces that undergo dramatic changes in temperature like gas turbines or airplane engine parts. They are thermally insulating and usually composed of oxides. YSZ is used as a TBC in diesel engines and gas turbines, applied using plasma spraying. Other choices for TBCs are mullite, alumina, ceria, metal-glass composites, rare earth zirconates, and rare earth oxides. Because the rare earth elements are also good luminescent activators and TBCs perform well at high temperatures, the TBC process may prove useful in terms of luminescent tagging for cladding.

Clarke and Gentleman [2017cla] incorporated luminescent compounds into the crystal structure of a TBC in order to directly measure the interface temperature as well as other locations in the TBC. The study required that the luminescent ion occupy one or more of the lattice sites in the crystal structure of the coating material. The coating materials used were yttria-stabilized zirconia (YSZ) and gadolinium zirconate (GZO)—each were able to incorporate rare earth ions as substitutional ions. In addition to being able to incorporate the luminescent ions, YSZ and GZO also contain oxygen vacancies which helps stabilize the luminescent properties by limiting the susceptibility to oxygen quenching. The first choice chromophore was Eu<sup>3+</sup> in YSZ because it is capable of luminescent at temperatures over 1000°C. However, of note is that while Eu<sup>3+</sup> can emit at high temperatures, the lifetime of the luminescence greatly decreases at high temperatures. This study aged Eu-doped YSZ for different lengths of time at 1425°C. It was found that there was no detectable effect on the luminescence

spectrum from the  $\text{Eu}^{3+}$  ions in YSZ. To further test the stability of the luminescence, the coatings went through cycling tests between room temperature and  $1150^{\circ}\text{C}$ . All of the coatings with a  $10\text{ }\mu\text{m}$  thick sensor layer at the TBC/bond-coat interface survived at least 400 cycles. The technique that this study applies, and the research it has offered is promising for use in the hostile environment of a reactor.

#### 4.5. Plasma Electrolytic Oxidation coatings

Plasma electrolytic oxidation (PEO) is one potential process for photoluminescent tagging on metal. The process of PEO is similar to anodizing where a layer of oxide is grown on the surface of a valve metal by the application of electrical potential while immersed in an acidic electrolyte. However, PEO uses higher voltages to achieve plasma discharges through the dielectric layer of the newly formed oxide coating (Figure 6). A coating of  $40\text{ }\mu\text{m}$  can be formed in approximately one hour. The technique requires coating on a valve metal surface. Examples of valve metals are Al, Mg, Ti, Zr, Ta, and Nb. A potential positive about this technique is that it also creates a hard outer layer ( $\sim 17\text{--}22\text{ GPa}$  for coatings on alpha alumina), acting as a protective barrier resistant to wear and corrosion. These coatings also have good chemical stability, and the composition of the coating can be modified in three different ways: alloy doping, electrolyte doping, and pore-filling. However, it is clearly visible, requires specific metals to adhere to, and can be expensive to produce. Although this process would not be applicable to nuclear fuels directly, Zr is the base metal for most fuel claddings, and therefore PEO coatings may be applicable in certain locations.

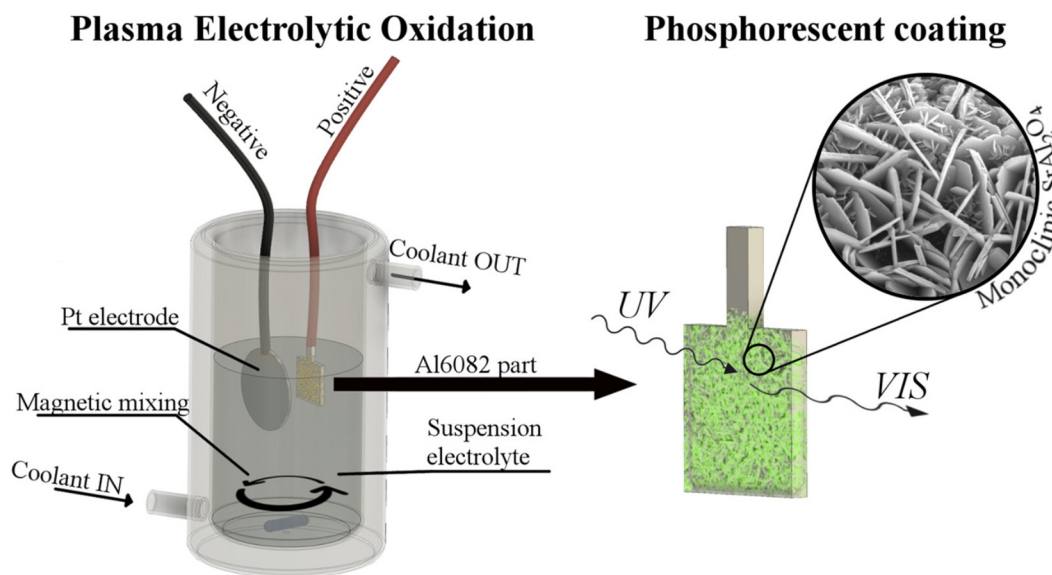


Figure 6. Graphical representation of preparation and characterization of the physical properties of the long afterglow luminescent PEO coating [2018bit].

Bite and others developed a method of using plasma electrolytic oxidation (PEO) of  $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ ,  $\text{Dy}^{3+}$  on 6082 Al [2018bit]. This method created a  $\sim 40\text{ }\mu\text{m}$  coating that was both phosphorescent and protective (Figure 7). The phosphorescent coating exhibited a long afterglow in a broad spectral

distribution at room temperature. The phosphorescence of this compound was found to be tunable, by increasing the Sr/Al ratio to  $\text{Eu}^{2+}$  emission shifts to longer wavelengths [2015dut].



Figure 7. The surface of 6082 Al before (a) and after the PEO process (b), as well as observed green afterglow luminescence from the PEO coating after UV irradiation (c) [2018bit].

A similar technique was used by Stojadinovic and others [2016sto] where  $\text{Eu}^{3+}$  doped  $\text{ZrO}_2$  coatings were formed using PEO on zirconium in a  $\text{Eu}_2\text{O}_3$  powder containing electrolyte. These same processes have been used to dope zirconia with  $\text{Sm}^{3+}$ ,  $\text{TiO}_2$  with  $\text{Eu}^{3+}$ , and  $\text{Nb}_2\text{O}_5$  with  $\text{Sm}^{3+}$ . Considering that the materials involved in this process can be costly, Zolotarjovs and others worked to minimize cost of materials by producing luminescent coatings using a PEO pore-filling technique, rather than coating the whole sample (Figure 8 ) [2016zol]. The study first produced a porous alumina coating on the aluminum substrate, and then filled the pores with the dopant before forming the final luminescent PEO coating. In addition to decreasing cost, it is possible that this technique would be less visible to those unaware of the tagging.

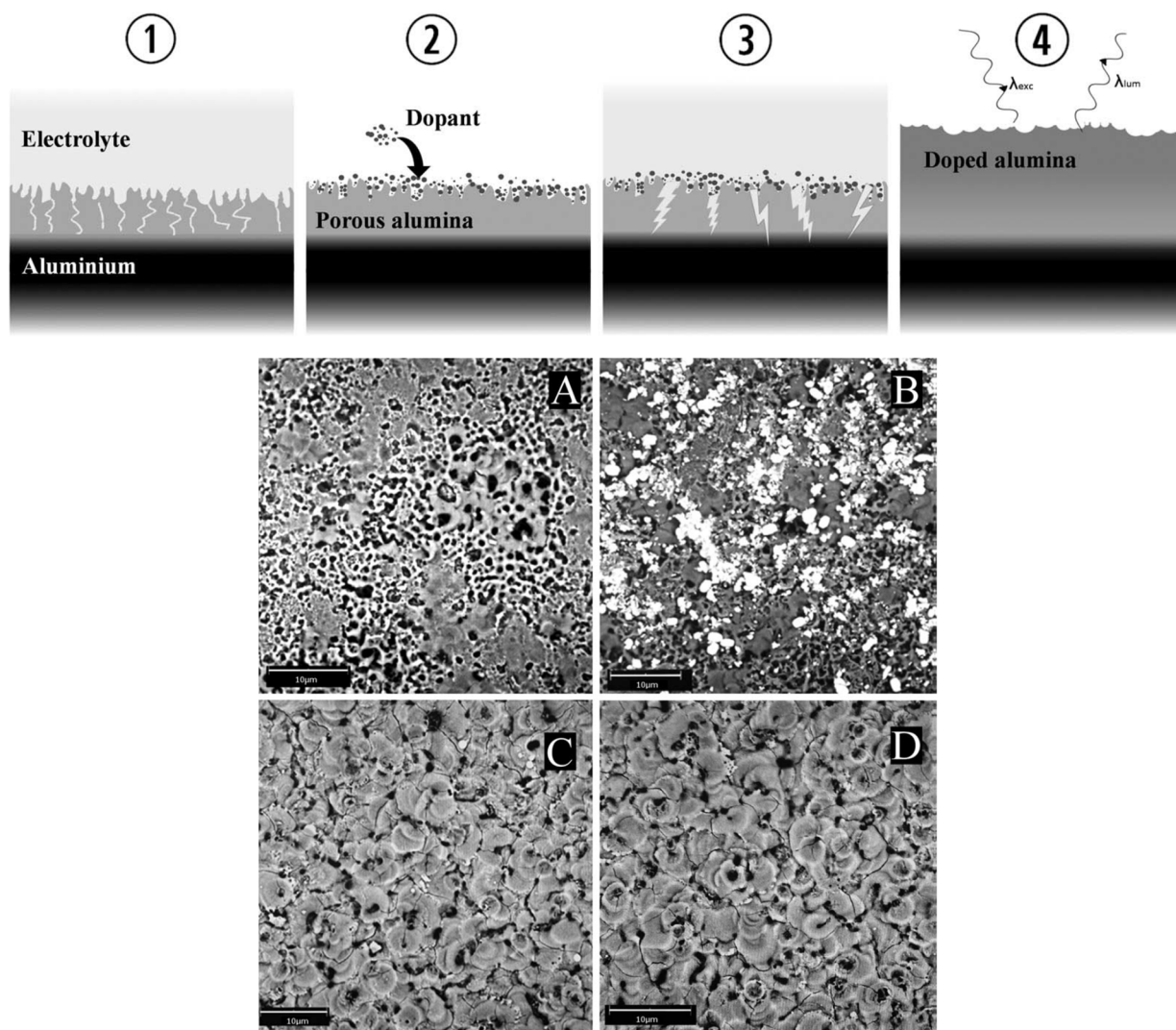


Figure 8. Schematic illustration with coordinating SEM images. 1) porous alumina coating preparation, 2) filling alumina pores with dopant particles, 3) PEO process, 4) final doped alumina coating. A) clear pores after first stage, B) pores filled with  $\text{Eu}(\text{OH})_3$  after second stage, C) PEO ceramic coating after third stage with Eu, D) PEO ceramic coating without Eu [2016zol].

## 5. Comparison of the attributes of the tagging techniques

Luminescent tags show considerable promise for nuclear fuel applications, but additional exploration and testing will be necessary to fully capture the effects on fuel performance, persistence in a nuclear reactor environment, and ability to detect the tag during manufacture and after interdiction. A summary of this literature review is presented in Table 2 to capture a qualitative representation of the author's current understanding of specific luminescent techniques. (Note this is not the same as a more formal TRL or MRL assessment; this table uses a simple 1-2-3 scale to avoid any ambiguity with TRLs and MRLs.)

Table 2. Stoplight chart summarizing various tagging-relevant attributes of interest vs. the five application methods.

Attribute of the luminescent tag	Dye	Paint	Thin Films	Thick Films	PEO
Ease of luminophore active ingredient production or attainment	3	2*	3	3	3
Ease of Application	3	3	2*	2	2
Ease of Detection	3	3	3	3	3
Persistence over time (at room temperature conditions)	3	3*	3	3	3
Persistence in a nuclear reactor environment (radiation, 300°C H <sub>2</sub> O)	1	2*	3*	2*	2*
Compatibility with Metallic Uranium Fuel (e.g. LEU-10Mo)	1	2*	3	2*	1
Compatibility with Oxide Uranium Fuel (UO <sub>2</sub> )	1	2*	2*	2*	1
Compatibility with Cladding (e.g. Zircaloy)	2	3	3	3	3
Compatibility with Other Metals	2	3	3	3	2
Compatibility with Other Materials	3	3	2*	2*	1
Ability to Conceal Tag	3	3	2	1	1
Multifunctionality (corrosion detection, protective, scannable, etc.)	3	3	2	3	3
Ability to Produce Fine Detail	3	3	3	2*	2*
Permutations Available	3	3	3	3	3

\*=more research is necessary, the choice of luminescent compound greatly affects this, or prohibitively expensive.

Stoplight Chart Legend	
1	This is not possible or compatible, or there is no work on this subject.
2	With additional research or development, this may be possible, or there is a lot of variability in the results.
3	This is something that has been done or studied before, is very likely to succeed, or is compatible fuel or cladding.



## 6. Discussion: Considerations for nuclear tagging applications

Sections 4 and 5 (the tagging manufacturing routes and the stoplight chart) require more explanation to crosswalk to the realm of uranium tagging and forensics. These notes now follow.

Major considerations for the utilization of luminescence for tagging are the ease of use and cost. The choice of luminophore significantly affects the cost and the ease of access. For example, dyes use readily available organic compounds. Because these organic compounds are used often for biologic tracing and medical purposes, there is an abundance of research on the use and tunability of each compound (fluorophores.org being one major example). Valeur and Berberan-Santos list a few of these databases and even places to purchase the compounds in their book [2012val]. These databases would be a good starting source if dyes were the final decision on taggant. However, the inorganic compounds are a bit more complicated in terms of “ease of production.” If an inorganic compound were chosen for a paint application, the production of the paint is somewhat involved. Particles of the compound would be purchased and then suspended in paint, which is time consuming and a difficult process. While the attainment of the inorganic compound may be relatively easy or inexpensive, the process to produce the final paint is not so simple. Films and PEO coatings are simpler, as rather than suspending particles in an epoxy or paint, the luminophore is instead doped into the process. Doping the electrolyte with a luminophore for a PEO coating appears relatively simple, but additional testing is necessary to confirm this notion. Bite and others purchased analytical grade compounds, mixed them with the electrolyte, and proceeded with the PEO process within the span of approximately 1 hour [2018bit]. This appears to be a relatively straightforward process from purchase to production. The variability in ease of attainment and production of the luminophore largely depends on what compound and what application is chosen.

If the simplicity of the tagging fuel was of highest priority, then intentionally oxidizing metallic uranium might be the best candidate for this application. The fuel is already uranium metal, therefore intentionally oxidizing it requires no external compounds, paints, or epoxies. This taggant is tough in terms of radiation exposure, persists over time, and likely can be done in relatively fine detail. However, there is radioluminescent noise to deal with as well as considering naturally oxidizing fuel fluorescence. Painting a luminescent coating onto cladding is expected to be simple, and the same ease is expected with a dye. Merunga and others show that a printer can be used to apply the paint in any pattern necessary [2012Mer]. The ease of application varies depending on what kind of thin or thick film application is chosen. As mentioned previously, spray pyrolysis may be the simplest as it does not require the item to be under vacuum.

Ease of measurement or ease of detection is also important for tagging applications. In general, ease of detection would be considered something that fluoresces or phosphoresces in the visible light spectrum when hit with a UV or “black” light. Whether the detection has to occur in the dark or can be seen with the unaided eye during the day depends on the choice of luminescent compound. The range in brightness varies, just as many of the properties vary as previously mentioned. More research is necessary in order to understand how much a post-irradiation examination hot cell or shielding could impact the ability to detect the luminescent tagging due to the refraction caused by the shielding material. Importantly, all of these tagging techniques have compounds available that radiate in the visible spectrum, depending on the source of excitation. If the combination of factors leads to choosing a luminescent compound where the emission falls outside of the range of human perception, it is

possible to use goggles that filter the light to aid visualization. Another option would be to use what Liu and others [2021liu] created: an ultra-compact smartphone fluorescence microscope. This pocket-sized scope was designed mostly with biology in mind, but it could work for other applications. Whether using this pocket scope or an unaided eye, this technique could prove to be relatively easy and inexpensive to use, once the tagging process has occurred.

In terms of persistence under ionizing radiation, oxidizing metallic uranium is clearly a good fit. However, if other options are under consideration, then understanding how luminescence interacts with radiation is paramount. One study by Vujčić et al. [2018vuj] sought to measure the effects of gamma radiation on a  $\text{YPO}_4:\text{Pr}^{3+}$  phosphor/scintillator. The  $\text{YPO}_4$  matrix had good optical and physical properties like large indirect band gap ( $\sim 8.6$  eV), high dielectric constant ( $\sim 7\text{--}10$ ), refractive index ( $\sim 1.72$ ), high melting point ( $\sim 1600^\circ\text{C}$ ). There are three major forms of radiation damage on the scintillators: a decrease in the attenuation length of the crystal, phosphorescence leading to readout noise, and finally reduced light output caused by scintillation-mechanism damage. This study found that with radiation increase from 0.25 MGy to 4 MGy, so too does the particle size increase. Also, the luminescence intensity rapidly decreases with the gamma radiation exposure. In another study on the effects of radiation on ceramic phosphors, Weeden-Wright and others tested the sensitivity of the luminescence of Eu doped lanthanum zirconate [2013wee]. The radiation exposures were X-rays and protons, and a much lower dose than the above study. However the important finding was that the effect of radiation depends on the phosphor. The study found that the Eu doped lanthanum zirconate luminescence was not particularly sensitive to the radiation sources and exposures. However, when another phosphor was added to the zirconate along with the Eu doped lanthanum, the radiation did have a negative effect on the luminescence. This subject will need further investigation if luminescence tagging will apply in a reactor.

Another consideration specific to luminescence in reactor conditions is whether the compound used is radioluminescent. There are compounds as mentioned above that can withstand radiation over time, but teasing out the intentional luminescence from the radioluminescent noise may prove difficult. More research on the radioluminescence of the chosen compound would need to be conducted before moving forward with cladding or fuel applications.

There are many luminescent options available, but choosing which to use depends on the application. For example, compounds doped with lanthanides would not do well in locations where the tagged material is exposed to the hot water of a reactor because lanthanides are especially soluble in water. However, because of this solubility, the lanthanides could act as a tracing agent in downstream processes if the fuel or clad were reprocessed. Depending on how much taggant was used, the lanthanides could possibly be measured downstream, not by the luminescence but rather by the concentrations. The ability to measure the taggant downstream would be highly dependent on the “headspace” available for that taggant. In other words, if the specific taggant already exists as a chemical species in the fuel or cladding (including as a fission product produced during in-pile exposure), measurement of this taggant would depend on the ability to discern the additions from the background composition.

Several other options that were evaluated in this review have contrasting properties that may or may not be sufficient for use in nuclear applications. SrAl phosphors are prone to hydrolysis, and their luminescent properties gradually deteriorate [2014ane]. ZnS and CdS are inorganic pigments that are

colorless in sunlight but fade when exposed to UV rays. ZnS doped with Cu or Co will not be very bright and has a shorter afterglow than SrAl phosphors according to 2010van. Sulfide-based phosphors are sensitive to CO<sub>2</sub> and moisture, and are also chemically unstable according to [2014ane]. ZnO coatings are sensitive to oxygen concentrations in the ambient atmosphere. The alumina based luminophores are tough and protective, but if hiding the taggant is important, they may not be the best choice. Although the options are numerous, the pros and cons of each must be considered against the environment, operating lifetime, and detection feasibility.

Similar to the environment having an effect on the luminescent compound, so does the chosen substrate. PEO coatings can only be applied to valve metals, so they are not compatible with uranium fuel or with other materials. However, paints and dyes are compatible with other materials, but the organic compounds in dyes cannot withstand the radiation exposure from uranium fuel, be it metallic or oxide, or the temperatures of a nuclear reactor. While the luminescent compounds in paint may persist well over time in room temperature conditions, the actual paint may have issues adhering to the surfaces of some metals or materials for long periods of time. Thin films other than UO<sub>2</sub> work well on most metals and other materials, but more research would be necessary on how they would work on oxide or ceramic fuels. Thick films on zirconium have been tested and have proven to be photoluminescent, and thus would be a good choice for cladding. However, thick films on uranium fuels, as far as this review has found, have not been researched. To best understand the compatibility of thin and thick films on uranium fuels, additional testing would be necessary.

If narrowing choices of application technique and luminescent compound by the ability to be concealed, produce fine detail, and be multifunctional, then painting the surface of the object would be excellent. Paint can be printed in very fine detail in a clear substance that could also be scanned as a QR code. The luminescent compound in paint is tunable and there are nearly endless permutations available. Dyes are equally as adaptive for detail and concealment. Dyes are also excellent for showing if changes in pH or corrosion are occurring. PEO coatings are not ideal for concealment as they produce an oxide layer on the surface. However, more research into the pore-filling technique from Zolotarjovs and others may prove the technique to be more concealable [2016zol]. Thin and thick films are tunable and have many permutations available. Thick films can provide a protective coating and even help with heat resistance. As mentioned throughout this report, there are many options available, and the end-use scenarios will need more research and development.

## **7. Conclusions**

The goal of this report was to understand the use of luminescent tagging for fuel and cladding, but there are many options outside of these. The use of photoluminescence in tagging has a very broad application where, depending on the compounds and the technique, the options are endless. There is a technique and compound for most every application; however, each has its own limitations. Much more research is necessary in order to consider photoluminescent tagging as an option. First, a baseline analysis of the naturally occurring luminescence in the environments in the entire nuclear lifecycle, including natural background. From there a more analytical exploration of the available luminophores and applications techniques, involving modeling and research efforts, should follow.

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